



Structural and associational aspects of binary and single polar liquids in non polar solvent under high frequency electric field

S K Sit, N Ghosh, U Saha and S Acharyya

Department of Physics, Raiganj College, Raiganj, Uttar Dinajpur-733 134,
West Bengal, India

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Abstract : The structural and associational aspects of binary (jk) polar mixtures of N,N dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) together with a single (j or k) N, N diethyl formamide (DEF) and DMSO in nonpolar solvents (l) are studied in terms of their high frequency (hf) conductivities. The relaxation times τ 's and dipole moments μ 's of the solutes under Giga hertz electric field at various temperatures are estimated from the measured real and imaginary parts of hf dielectric constants at different weight fractions of polar solutes. The variation of τ_{jk} 's with mole fractions x_k 's of DMSO in DMF and C_6H_6 reveals the probable solute-solute molecular association around $x_k = 0.5$ of DMSO. The solute-solvent molecular association begins at and around 50 mole% DMSO in DMF and continues upto 100 mole% DMSO. The concentration and temperature variations of τ_{jk} of these protic liquids are in accord with the information of variation of τ_{jk} of jk polar mixtures with x_k 's of DMSO. Thermodynamic energy parameters are also obtained from Eyring's rate process equation with the estimated τ 's to support the molecular associations. The slight disagreement between the theoretical dipole moments μ_{theo} 's from the bond angles and bond moments is noticed with the measured μ 's in terms of slopes of concentration variation of hf conductivity curves at infinite dilutions and τ 's. This indicates the temperature dependence of mesomeric and inductive moments of different substituent groups of the molecules.

Keywords : Dipole moment, relaxation time, associational aspects

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The dielectric relaxation mechanism of a polar-nonpolar liquid mixture under the microwave electric field is of special interest [1,2] for its inherent ability to predict the associational aspects of polar solutes in nonpolar solvents. An investigation was, however, made on ternary solution of binary polar liquids in which both or even one of them are aprotic [2,3] to study various types of weak molecular associations by polar liquids in

nonpolar solvents. We are, therefore, tempted further to consider more mixtures of binary aprotic polar liquids like N,N dimethyl formamide (DMF) and dimethyl sulphoxide (DMSO) together with a single aprotic polar liquid like N,N diethyl formamide (DEF) and DMSO in C_6H_6 and CCl_4 [4–6] respectively. DMSO, DMF and DEF are very interesting liquids for their wide application in medicine and industry. They also act as building blocks of proteins and enzymes. The concentration variation of the measured real ϵ'_{ijk} , ϵ'_{ij} or ϵ'_{ik} and imaginary ϵ''_{ijk} , ϵ''_{ij} or ϵ''_{ik} parts of hf complex dielectric constants ϵ^*_{ijk} , ϵ^*_{ij} or ϵ^*_{ik} of jk , j or k polar solutes in nonpolar solvents are used to detect the weak molecular interactions among the molecules [7] at a single or different temperatures under nearly 3 cm wavelength electric field. The τ_{jk} of jk polar mixtures as well as τ_j 's or τ_k 's of j or k polar solutes in a nonpolar solvent were estimated from :

$$K''_{ijk} = K_{\omega_{ijk}} + \frac{1}{\omega\tau_{jk}} K'_{ijk}, \quad (1)$$

where $K''_{ijk} = \frac{\omega}{4\pi} \epsilon''_{ijk}$ and $K'_{ijk} = \frac{\omega}{4\pi} \epsilon'_{ijk}$ are the imaginary and real parts of complex hf conductivity K^*_{ijk} [8]. The other terms carry usual significance as presented elsewhere [2]. The τ_{jk} 's are estimated from the slopes of the linear variations of K''_{ijk} against K'_{ijk} of eq. (1). The linearity of eq. (1) is tested by the correlation coefficients and the errors involved in the measurement of τ 's are within 5%. τ_{jk} 's are then plotted with different mole fractions x_k 's of DMSO at various experimental temperatures as shown in Figure 1

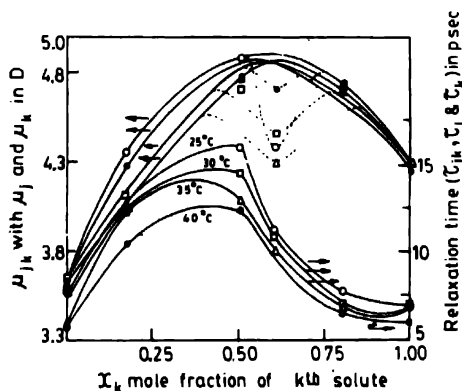


Figure 1. Variation of τ_{jk} and μ_{jk} of DMF–DMSO mixture in C_6H_6 against mole fraction x_k of DMSO with τ_j and τ_k and μ_j and μ_k of DMF and DMSO respectively at different temperatures : (○) at 25°C, (□) at 30°C, (Δ) at 35°C and (●) at 40°C.

The formation of dimer is responsible for the gradual rise of τ_{jk} from τ_j of DMF at $x_k = 0$ to $x_k = 0.5$ and then its rapid fall to τ_k due to rupture of dimerisation and self association [4]. The estimated τ 's are slightly larger than those of Gopalakrishna's method [9]. But τ 's from conductivity measurement are much more reliable as they provide microscopic relaxation times [10].

The energy parameters due to dielectric relaxation process were then obtained in terms of measured τ from the rate process equation of Eyring *et al* [11] :

$$\tau_s = \frac{A}{T} e^{\Delta F_r / RT}$$

$$\text{or} \quad \ln(\tau_s T) = \ln A' + \frac{\Delta H_r}{RT}, \quad (2)$$

where $A' = Ae^{-\Delta S_r / R}$.

Eq. (2) is a straight line of $\ln(\tau_s T)$ against $\frac{1}{T}$ as seen in Figure 2 having intercepts and slopes to yield the entropy of activation ΔS_r , enthalpy of activation ΔH_r and free energy of activation ΔF_r due to dielectric relaxation. The values of $\gamma \left(= \frac{\Delta H_r}{\Delta H_\eta} \right)$ for all the liquids

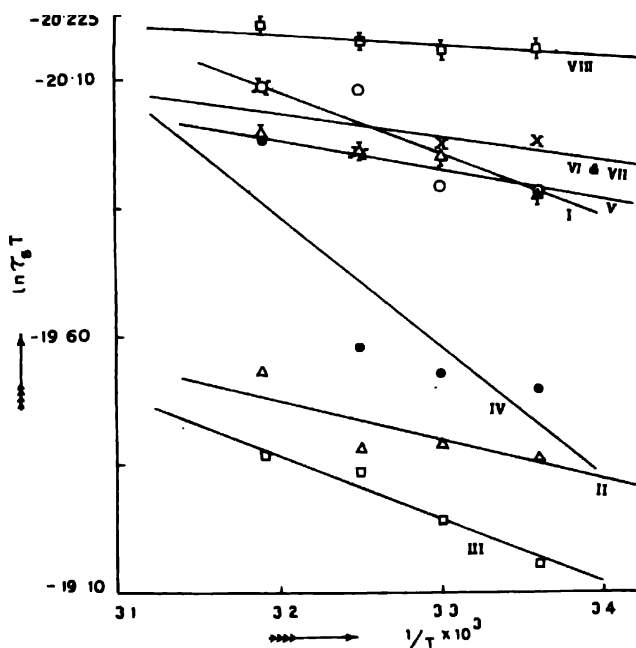


Figure 2. Variation of $\ln(\tau_s T)$ against $\frac{1}{T}$ of binary and single polar solutes in nonpolar solvent I-DMF + 0 mole% DMSO in C_6H_6 (O), II-DMF + 17 mole% DMSO in C_6H_6 (Δ), III-DMF + 50 mole% DMSO in C_6H_6 (\square), IV-DMF + 60 mole% DMSO in C_6H_6 (\bullet), V-DMF + 80 mole% DMSO in C_6H_6 (\blacktriangle), VI-DMF + 100 mole% DMSO in C_6H_6 (X), VII-DMF + 80 mole% DMSO in CCl_4 (\odot), VIII-DMSO in CCl_4 (\bullet).

except DMSO in CCl_4 are greater than 0.55, as obtained from the slope of the linear relation of $\ln(\tau_s T)$ with $\ln \eta$ indicating them as solid phase rotators in solvent environment. η is the

coefficient of viscosity of solvent. ΔH_η due to viscous flow of the solvent is obtained from slope of $\ln(\tau_r T)$ against $\frac{1}{T}$ and known γ . Again, ΔH_η are greater than ΔH_r for all the mixtures except 0, 50 and 60 mole% DMSO in DMF and C_6H_6 . The difference in ΔH_r and ΔH_η is due to the involvement of various types of bondings which are either formed or broken to some extent, depending on the temperature and concentration of the system. The negative values of ΔS_r 's for all the systems except 0 and 60 mole% DMSO in DMF and C_6H_6 indicate the existence of cooperative orientation of the molecules arising out of steric forces to yield more ordered states while the reverse is true for positive ΔS_r 's. Although, ΔF_r 's in all cases are almost constant at all temperatures, they increase with x_k of DMSO from $x_k = 0.0$ to $x_k = 0.5$ and then decrease gradually to $x_k = 1.0$ signifying the maximum dimerisation of DMF-DMSO mixture around $x_k = 0.5$. The formation of dimer causes larger molecular size and hence, the energy needed for rotation in the relaxation process is higher.

The hf conductivity K_{ijk} as a function of weight fraction W_{jk} is given by

$$K_{ijk} = \frac{\omega}{4\pi} (\epsilon'_{ijk}{}^2 + \epsilon''_{ijk}{}^2)^{\frac{1}{2}}. \quad (3)$$

Since $\epsilon'_{ijk} \gg \epsilon''_{ijk}$ eq. (1) can be written as

$$K_{ijk} = K_{\infty ij} + \frac{1}{\omega \tau_{jk}} K'_{ijk},$$

$$\text{or} \quad \left(\frac{dK'_{ijk}}{dW_{jk}} \right)_{W_{jk} \rightarrow 0} = \omega \tau_{jk} \beta. \quad (4)$$

Here, β 's are the slopes of $K_{ijk} - W_{jk}$, $K_{ij} - W_j$ or $K_{ik} - W_k$ curves respectively, which are linear with almost identical intercepts probably due to same polarity of the molecules [2]. The real part of hf conductivity, K'_{ijk} is again related to W_{jk} of jk polar solute dissolved in a nonpolar solvent (i) at temperature $T^\circ K$ [12] as

$$K'_{ijk} = \frac{\mu_{jk}^2 N \rho_{ijk} F_{ijk}}{3 M_{jk} k T} \left(\frac{\omega^2 \tau_{jk}}{1 + \omega^2 \tau_{jk}^2} \right) W_{jk}. \quad (5)$$

Differentiating eq. (5) with respect to W_{jk} and comparing the result at $W_{jk} \rightarrow 0$ to eq. (4), one obtains the following relation

$$\mu_{jk} = \left[\frac{27 M_{jk} k T}{N \rho_i (\epsilon_i + 2)^2} \cdot \frac{\beta}{\omega b} \right]^{1/2}. \quad (6)$$

to estimate μ_{jk} , μ_i or μ_k of the respective solutes. b is a dimensionless parameter in terms of estimated τ_{jk} , τ_i or τ_k given by :

$$b = \frac{1}{1 + \omega^2 \tau_{jk}^2}. \quad (7)$$

The other terms in eq. (6) carry usual significance [2]. All the μ 's are then plotted against different x_k 's of DMSO at each temperature as shown in Figure 1. It shows the gradual rise of μ_{jk} in the range $0 < x_k \leq 0.5$. It then decreases slowly in order to exhibit the convex nature of each curve with an abnormally low value of μ_{jk} around $x_k = 0.6$. This sort of behaviours of $\mu_{jk} - x_k$ curves (Figure 1) is explained by the fact that dimers are being formed from $x_k \geq 0$ to $x_k = 0.6$ causing increase of μ . The rupture of dimerisation *i.e.* self association occurs in higher concentrations in the range $0.6 \leq x_k < 1.0$ to yield lower values of μ 's. But around $x_k = 0.6$, all μ_{jk} 's are minimum indicating the possible occurrence of double relaxation phenomena in such mixtures to be studied later on. μ_{jk} together with μ_j and μ_k for each mixture of a fixed concentration are shown graphically only to observe their temperature dependence like $\mu_k = a + bt + ct^2$ with coefficients a , b and c as seen in Figure 3. The variation is concave with maximum depression at 17 mole% DMSO in DMF mixture. The depression gradually decreases upto $x_k = 0.6$ of DMSO in DMF and C_6H_6 probably due to solute-solute molecular association in the range $0 < x_k < 0.6$. The maximum

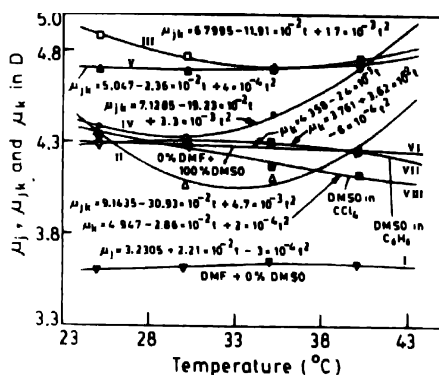


Figure 3. Variation of μ_j , μ_{jk} and μ_k of binary and single polar solutes in nonpolar solvent with temperature t in $^{\circ}\text{C}$

I—DMF + 0 mole% DMSO in C_6H_6 (∇),
II—DMF + 17 mole% DMSO in C_6H_6 (Δ),
III—DMF + 50 mole% DMSO in C_6H_6 (\square),
IV—DMF + 60 mole% DMSO in C_6H_6 (\bullet),
V—DMF + 80 mole% DMSO in C_6H_6 (\blacktriangle),
VI—DMF + 100 mole% DMSO in C_6H_6 (∇), VII—DMSO in C_6H_6 , (O), VIII—DMSO in CCl_4 (\blacksquare)

dimerisation is, however, inferred from low μ 's because of the larger molecular sizes as confirmed by high values of $\tau_s T / \eta \gamma$ (being proportional to volume of the rotating unit) for 60 mole% DMSO in DMF and C_6H_6 . As temperature increases the dipole-dipole interaction is weakened and the absorption of hf electric energy increases resulting in the rupture of dimer to yield high μ 's for smaller molecular species [10]. The slight convex nature of curves for 0 mole% DMSO in DMF and C_6H_6 and DMSO in C_6H_6 , along with almost straight line variation of 100 mole% DMSO in DMF and C_6H_6 and DMSO in CCl_4 (Figure 3) is probably due to solute-solvent molecular interaction of either DMF with C_6H_6 or DMSO with C_6H_6 and CCl_4 respectively as illustrated in Figure 4. The associations of DMF, DEF and DMSO in C_6H_6 can arise due to interactions of fractional positive charges of N and S atoms of the molecules with the π delocalised electron cloud of C_6H_6 ring as seen in Figure 4(i), (iii) and (iia) respectively. Again, one of C—Cl dipoles of CCl_4 , owing to more $-ve$ charge on Cl atom, interacts with the fractional

+ve charge of S-atom of DMSO (Figure 4 (iib)). The $\mu_{\text{theo}} = 4.55$ D of DMSO is, however, computed from available bond moments of 2.35 D and 1.55 D for $\text{S} \leftarrow \text{CH}_3$ and $\text{O} = \text{S}$ respectively, assuming the molecule to be planar one. The major contributions to μ_{theo} for DMF and DEF are due to 0.64 D and 0.78 D for $\text{N} \leftarrow \text{CH}_3$ and $\text{N} \leftarrow \text{C}_2\text{H}_5$ since the other common bond moments in them are the same with values of 0.3 D, 0.45 D and 3.10 D for $\text{C} \leftarrow \text{H}$, $\text{C} \leftarrow \text{N}$ and $\text{C} \equiv \text{O}$ respectively. Figure 4 (iv), however, shows a certain angle ϕ ($= 106^\circ$) between monomeric μ 's of DMF and DMSO to have $\mu_{\text{theo}} = 4.77$ D of dimer below $x_k = 0.6$.

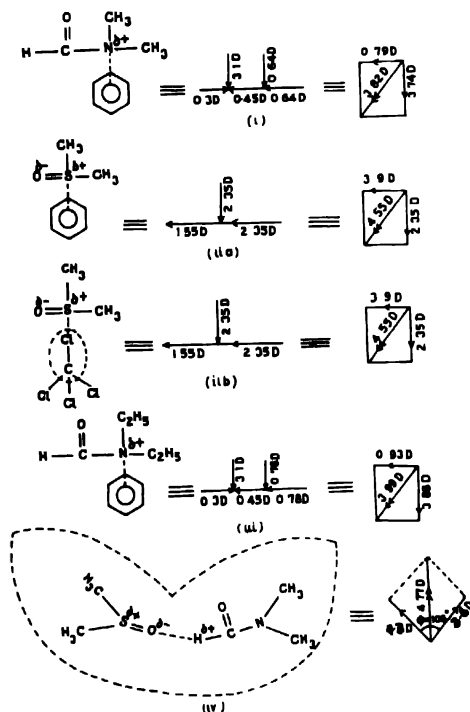


Figure 4. Conformational structures along with solute-solvent and solute-solute interaction of molecules (i) DMF in C_6H_6 , (ii a) DMSO in C_6H_6 , (ii b) DMSO in CCl_4 (iii) DEF in C_6H_6 , (iv) DMSO-DMF dimer.

The slight deviations of the μ 's from the μ_{theo} 's occur probably due to the presence of inductive and mesomeric moments of such molecules. This is also observed elsewhere [13]. The corrected μ 's obtained from the reduced bond moments of the substituent groups by factors $\mu_{\text{cal}}/\mu_{\text{theo}}$ establish the above facts at different temperatures, too. Thus the dielectric relaxation parameters from hf conductivity measurements offer a useful tool to arrive at the structural and associational aspects of the non-spherical polar liquids.

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